



Ultrafast Studies of Unimolecular Dissociation Rates of the Acetyl and Methyl Sulfonyl Radicals

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Gas Phase Photodissociation Dynamics

Multiple dissociation reactions: beyond concertedness
Unimolecular dynamics of intermediates:

- RRKM or nonstatistical dissociation
 - energy disposition of products:
among (partitioning) & within (IVR) products
 - **dissociation rates**
- Excited state dynamics

Condensed Phase Photochemistry

- Solution: faster relaxation
- Surface adsorbates:
unique substrate-mediated mechanisms

Biochemistry
Molecular Electronics
Laser Machining

Optical Control

- Medium-sized molecules
- "Leverage" - sequential reactions

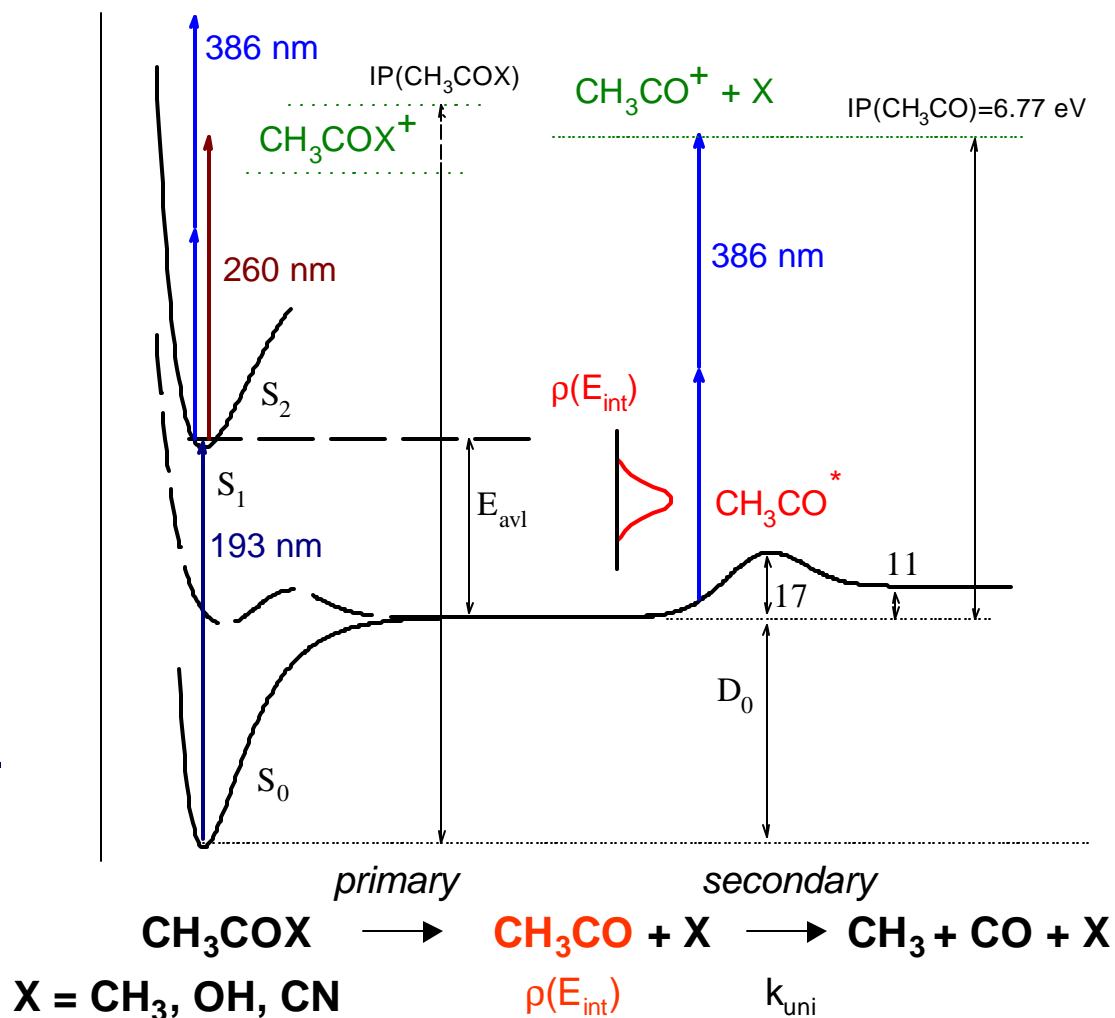
Atmospheric Chemistry:
Stable radical source



Multiple Dissociation Dynamics

Unimolecular Dissociation:

- Is it statistical, RRKM?
- $k_{\text{uni}}(E_{\text{int}}) = k_{\text{RRKM}}?$
- If nonstatistical,
 - is it inherent?
 - $k_{\text{uni}} > \text{IVR}$ (k_{uni} dependent?)
 - or depend on preparation?
 - precursor
 - excited state
- Clearest assessment when **both**
 - k_{uni} and E_{int} are measured





Ultrafast Photoionization Studies:

1) Acetyl - CH_3CO

- Benchmark multiple dissociation intermediate
 - ▶ extensively studied - energy partitioning determined
 - ▶ time-resolved - dissociation times
 - ▶ basis to assess how statistical ("RRKM-ness")
- Directly compare for **same excitation** conditions:
 - $k_{\text{obs}} = k_{\text{RRKM}}(E_{\text{int}})$? Need k_{obs} and E_{int}
 - ▶ product studies at 193 nm:
 - ▶ **deep UV fs photoionization**
- Various precursors: range of precision in E_{int} (acetyl)

Basic
Understanding

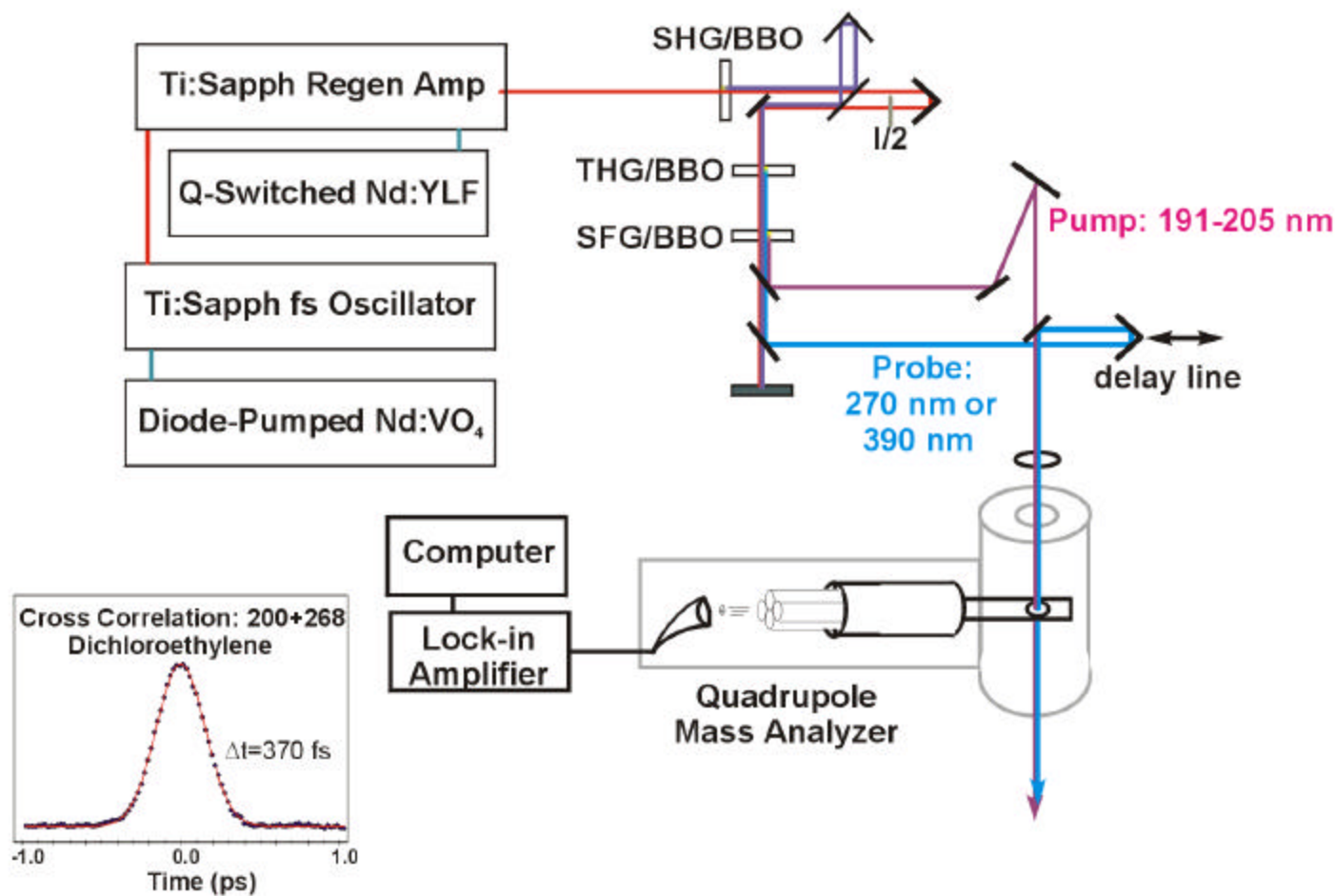
Application:
Stable Radicals

2) Methyl Sulfonyl - CH_3SO_2

- Not as well characterized (e.g., energy partitioning)
- Find precursor for source of stable radicals



Mass-Resolved Deep UV Femtosecond Photoionization Spectroscopy





Ultrafast Photoionization of the Unimolecular Dissociation of Acetyl Radical

Acetyl from Several Precursors:

Acetone (h_6 and d_6): S_2 Rydberg at 193 nm

- ▶ Extensively studied - energy partitioning (*North et al.*)
- ▶ Polyatomic fragments - imprecise $E_{\text{int}}(\text{acetyl})$

$k(\text{uni})_{\text{obs}}$ vs. k_{RRKM} : *acetyl dissociation rates not statistical*

Acetyl Cyanide and Acetic Acid at 193 nm

- ▶ Product studies at 193 nm
- ▶ Diatomic companion - precise $E_{\text{int}}(\text{acetyl})$

acetyl dissociation rates consistent with RRKM

Nonstatistical acetyl dynamics:

precursor dependent - NOT intrinsically non-RRKM

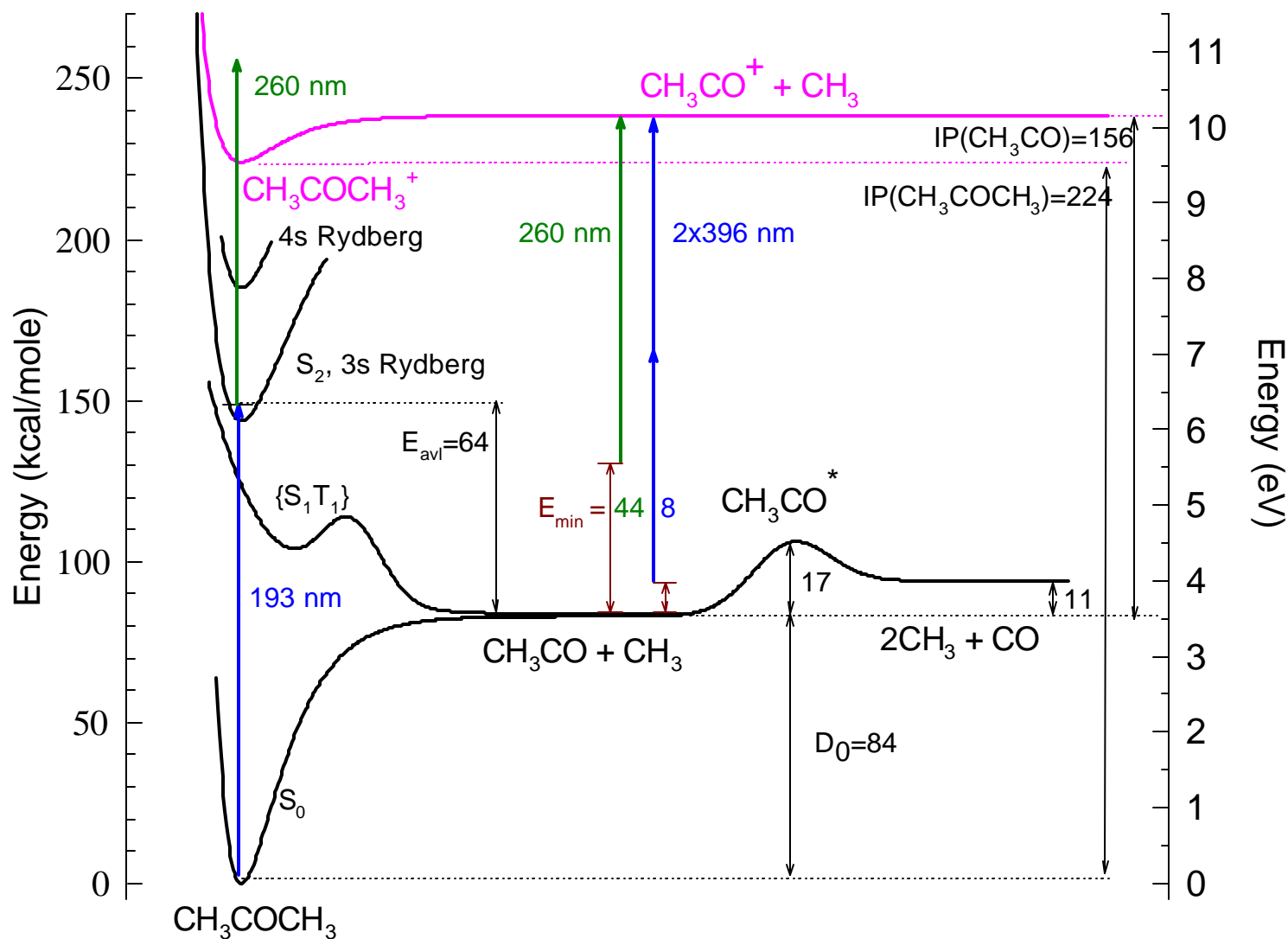


Very Brief History of Acetone Photodissociation at 193 nm

- S_2 , Rydberg state excited at 193 nm
- Product energies: PTS and spectroscopy
 - ▶ Numerous product internal energy studies, UV and IR : CH_3 and CO
 - ▶ $\langle E_T \rangle$ (16 kcal/mole) [North et al.] : better determined than $\langle E_{\text{int}} \rangle$
 - ▶ $E_{\text{int}}(\text{CH}_3)$ and $E_{\text{int}}(\text{CH}_3\text{CO})$ - not well determined: 12-17 kcal/mole
- **17 ± 1 kcal/mole barrier** for acetyl dissociation: PTS of acetyl chloride [North et al.]

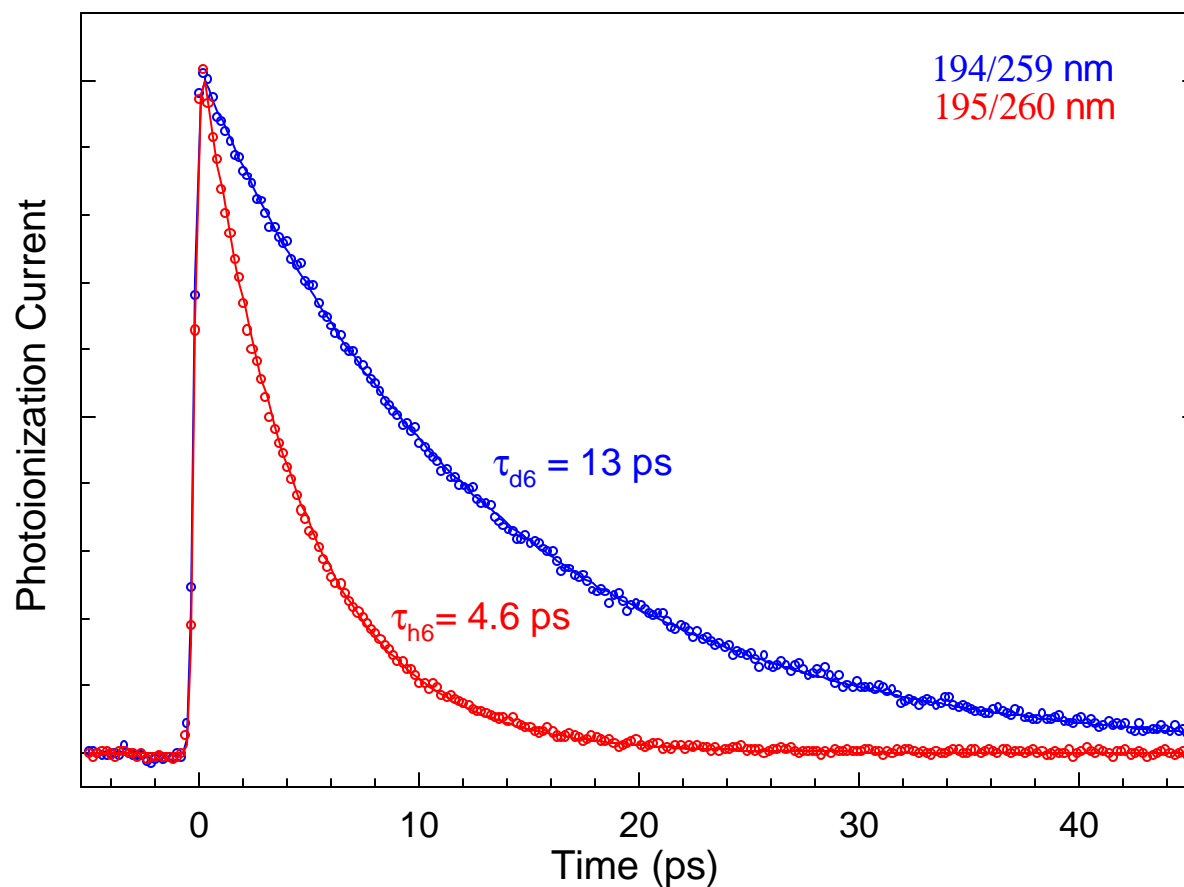


Acetone Potential Energy Surfaces





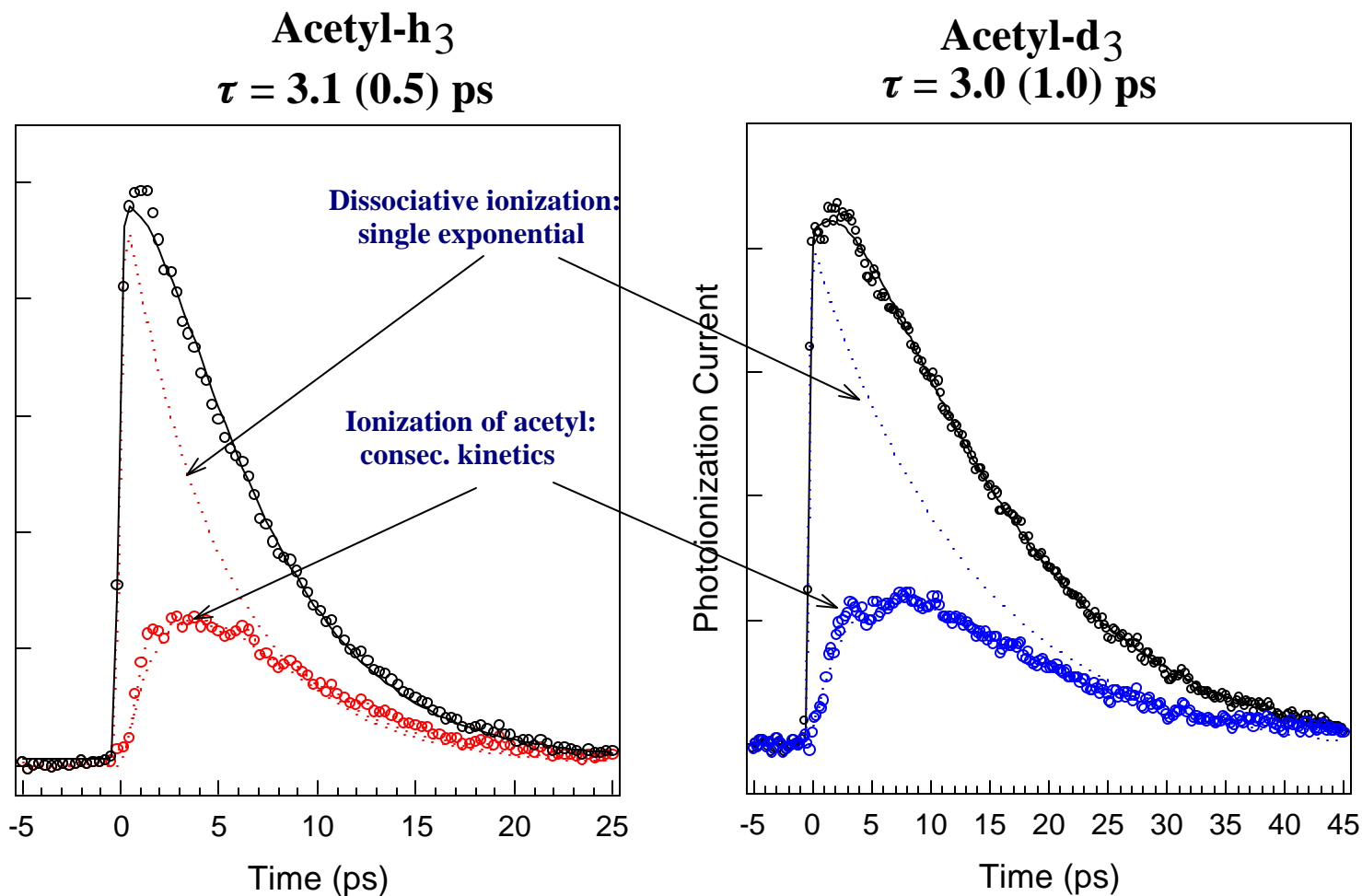
Primary Dissociation Dynamics Lifetime of S_2 State





Acetyl Dissociation Dynamics

195 + 2x390 nm





Summary of Ultrafast Results for S₂ of Acetone

- S₂ excited state lifetime is long and isotope dependent - why it's isotropic
- Acetyl unimolecular dissociation rate implies it's nonstatistical
 - ▶ simple comparison of k_{obs} and $k(E_{\text{int}})$ prevented by large uncertainty in E_{int}
 - ▶ $1/k_{\text{obs}} = 3.1$ ps: apparent $E_{\text{int}}(\text{CH}_3\text{CO}) = 25$ kcal/mole using RRKM rate:
 - inconsistent with standard energy partitioning (imp., BIM, stat.)
 - k_{obs} slower than expected (like other obs. nonRRKM for acetyl)
- Unambiguous determination of nonRRKM dissociation precluded by complexity of methyl group
- Find acetyl precursors with simple fragments & well determined internal energy

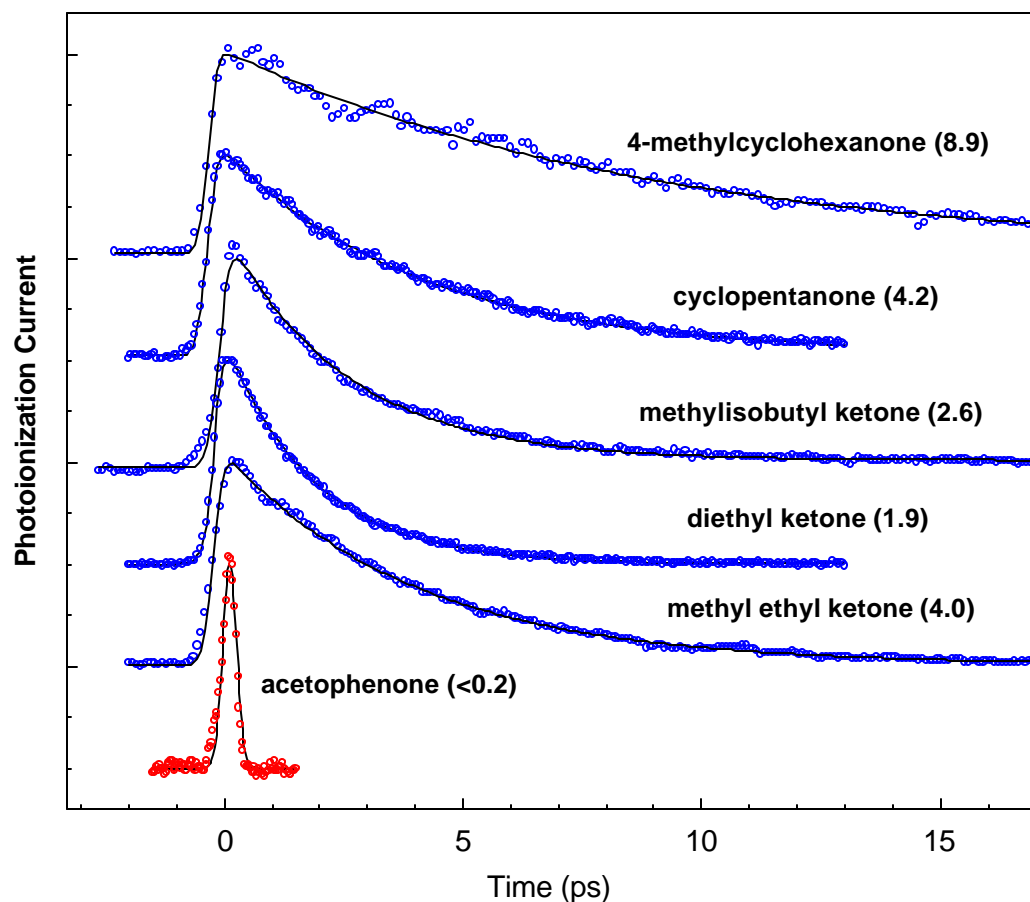
Hello, Acetyl Cyanide and Acetic Acid !



More Ketone Excited State Lifetimes

For 195-200 nm excitation:

- aliphatic ketones: excited state lifetimes are 2-9 ps
- prompt for acetophenone (aromatic ketone)





Acetyl Cyanide and Acetic Acid near 195 nm

Background and Previous Studies

(Horwitz et al. , North et al. and Guest and coworkers)

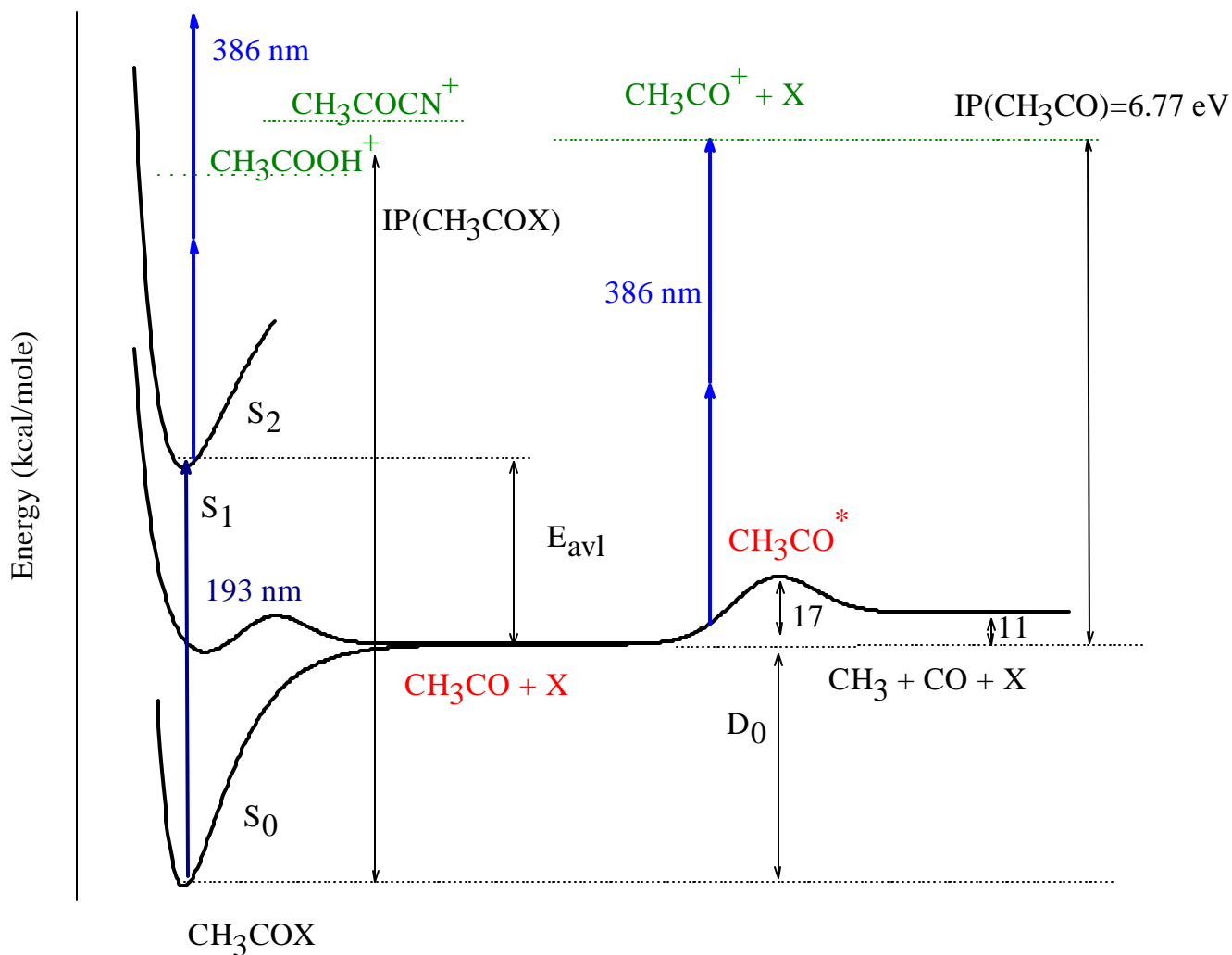
- Major primary dissociation channel: to acetyl + OH/CN



- Negligible product angular anisotropy
- Product energy distributions measured for diatomic fragments
 - ▶ internal state distributions (R and V) measured spectroscopically
 - ▶ translation energy distributions: Doppler for OD; PTS for CN
- Acetyl internal energy distribution determined for both precursors



Potential Energy Surfaces





Energetics and Product Energies

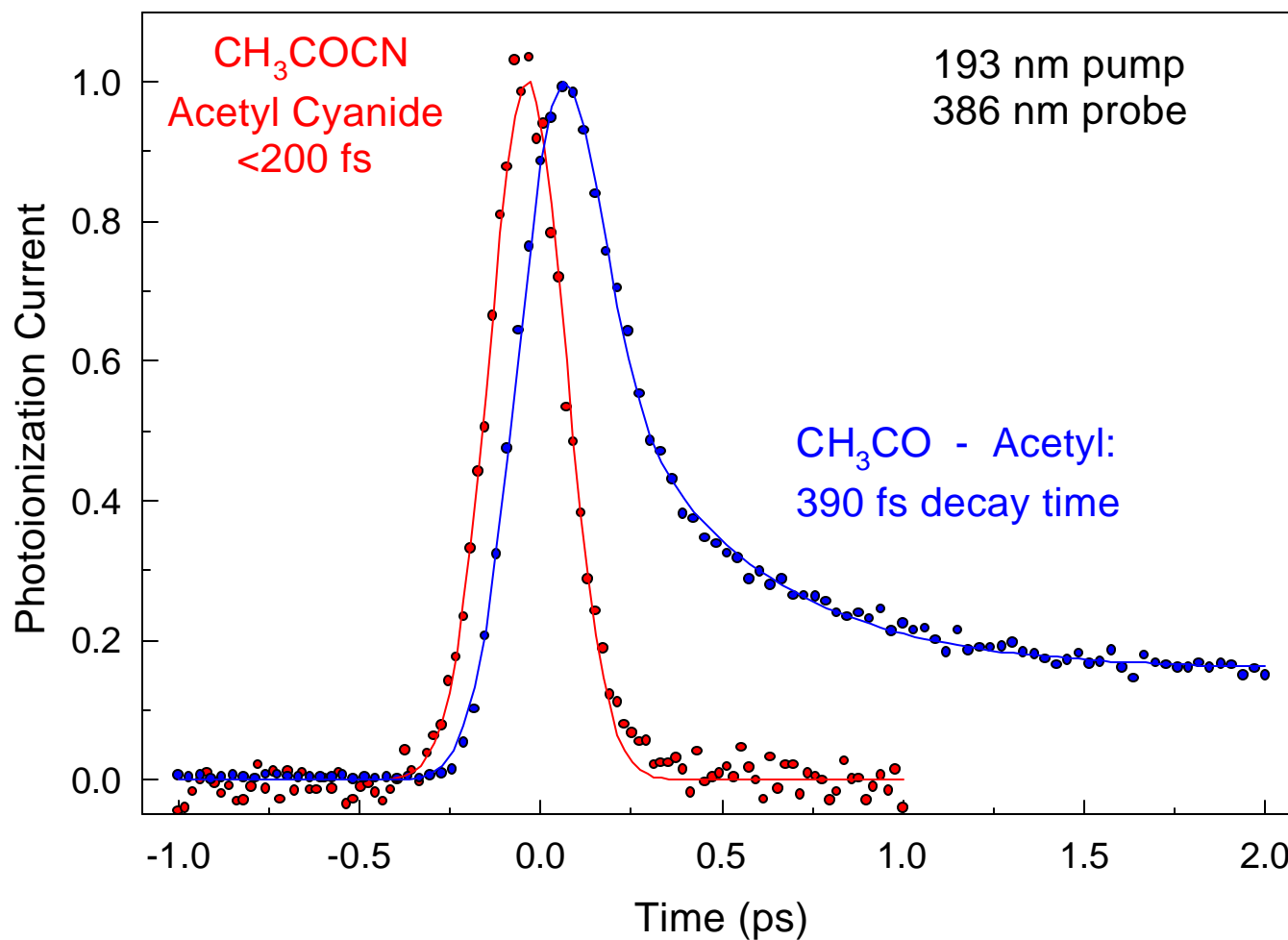
$\delta_{\text{exc}}(\text{nm})$ [kcal/mole]	E_{avl}	$\langle E_t \rangle$	$\langle E_r(X) \rangle$	$\langle E_v(X) \rangle$	$\langle E_{\text{int}}(\text{CH}_3\text{CO}) \rangle$
CH₃COOH (X=OH), $D_0=110$					
218 [131.2]	21.2	13.7	1.2	<0.2	4.9
200 [143.0]	33.0	14.5	1.4	<0.4	16.7
194 [147.7]	37.7	15.0 ^a	1.4	<0.5	20.8
CH₃COCN (X=CN), $D_0=102.2$					
193 [148.1]	45.9	7.2	3.6	1.2	33.9

a. $\langle E_t \rangle$ at 194 nm extrapolated from 200 and 218 nm results

Acetyl from acetone at 193 nm: $\langle E_{\text{int}}(\text{CH}_3\text{CO}) \rangle$
from product studies: 31-45 kcal/mole?
from k_{obs} via $k_{\text{RRKM}}(E_{\text{int}})$: 25 kcal/mole

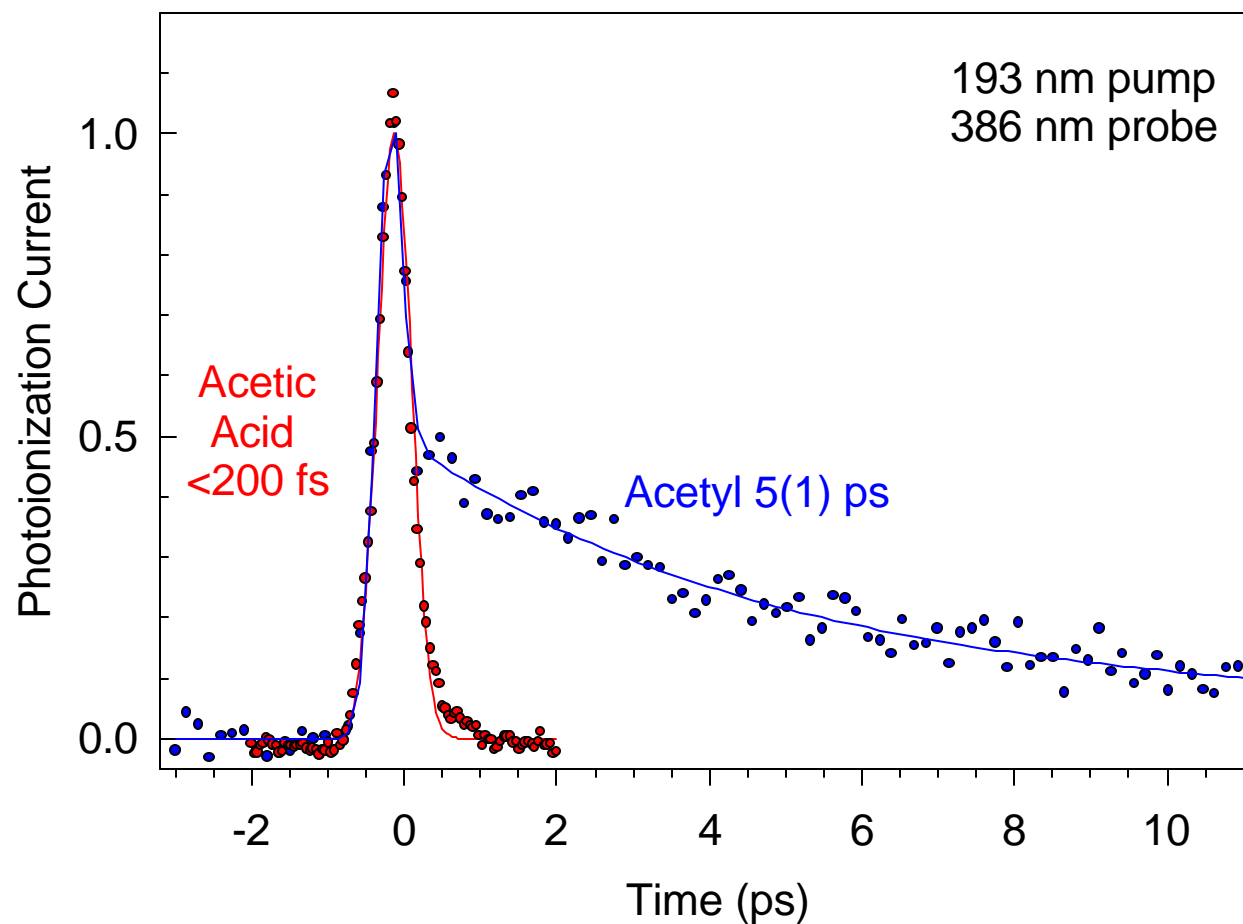


Acetyl Cyanide Photodissociation Dynamics





Acetic Acid Photodissociation Dynamics





What is the CH_3COCN Transition at 194 nm?

How is acetyl prepared? Does this affect dynamics?

- For acetone at 193 nm: predissociation from a Rydberg state
- For acetic acid at 200 and 218 nm: from excitation of a B^*7n transition
- For acetyl cyanide at 193 nm: *NOT* clear

Acetyl Cyanide Product Anisotropy and Excited State Lifetime

- No anisotropy observed ($\beta = 0$, [North et al.]):
 - ▶ suggested transition to Rydberg state - high anisotropy
 - ▶ low anisotropy obs. - rotational averaging for long lived excited state:
- Does not agree with our measured short excited state lifetime

Angular Product Distribution and Excited State Lifetime - In General

Isotropic: 1) long lived state - rotational averaging (S_2 acetone, S_1 ?)
2) fast but magic angle between transition moment and diss. bond
(S_1 acetone, DMSO, acetic acid and *acetyl cyanide*)

Anisotropic: fast



194 nm Transition Assignment for Acetyl Cyanide

Acetyl Cyanide Transition from Rydberg State Energy

Rydberg state energy: $E_{n,l} = IP - (13.606/(n - l)^2)$

- Ionization Potential of Acetyl Cyanide: 11.2 eV
 - ▶ No acetyl cyanide ions with 193 nm/257 nm
 - ▶ FTMS bracketing expts [McElvany & Baronavski]
- The 3s of acetyl cyanide, $E_{3s} = 7.82$ eV (158 nm):
 E_{3s} (acetone) agrees with observed: 6.30 eV (197 nm)
- 194 nm transition in acetyl cyanide **is not** to a Rydberg state.

VUV Spectra and Excited State Calculations for CH_3COCN

- Wiberg et al.: Time Dependent Density Functional methods
accurate excited state calculations of acetone, formaldehyde, and acetaldehyde
- G98 calculations for acetone and acetyl cyanide:
MP2 optimized structures, B3P86 functional: acetone results agree w/ spectra
- Measure VUV spectra of acetyl cyanide and compare with calculations

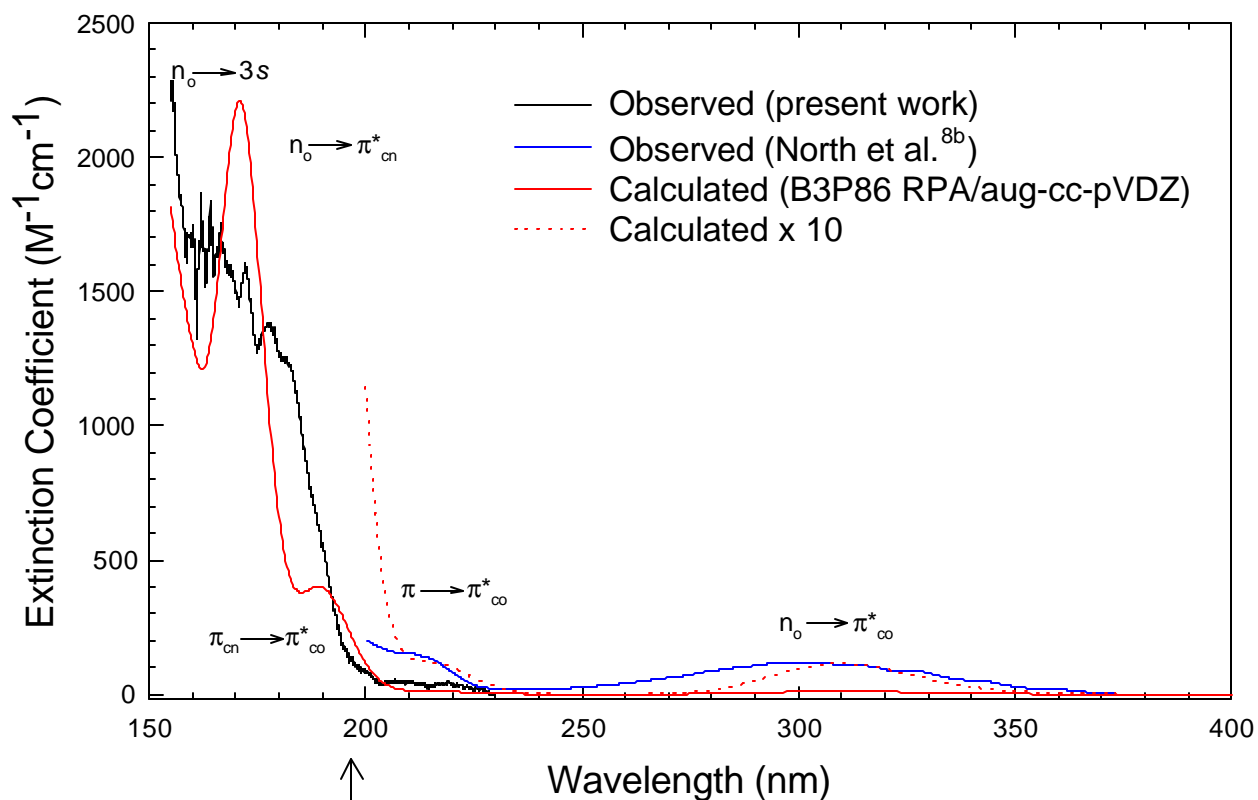


Results from Calculations and Spectra

- The calculated spectrum agrees well with our experimental spectrum
- The 193 nm absorption is due to a B* \rightarrow B rather than 3s \rightarrow n transition
 - ▶ Indicated by orbitals
 - ▶ The 3s Rydberg state is calculated to be at 7.57 eV
- Assignment consistent with higher IP and location of Rydberg
G94 calculation at MP2 level: IP(adiabatic) = 11.49 eV
- The transition moment for 194 nm band at 57E with respect to the CN bond
 - ▶ Results in $\mu = -0.22$, probably too small for North *et al.* to measure
 - ▶ Explains isotropic products with short lifetime
- Excitation for acetyl cyanide more similar to that for acetic acid (valence) than for acetone (Rydberg)



Calculated and Observed Absorption Spectra for Acetyl Cyanide



↑
We are here



Measured and Calculated Acetyl Dissociation Times

For both molecules, parent excited state is short-lived (<300 fs)

$\lambda(\text{nm})$	$\langle E_{\text{int}} \rangle (\text{kcal})$	Precursor	$\tau_{\langle E_{\text{int}} \rangle} (\text{ps})$	τ_{dist}	τ_{obs}
194.5	19.6	CH_3COOH	9.1	6.2	5 (1)
194.5	31.0	CH_3COCN	0.74	0.56	0.56
194.0	31.4	CH_3COCN	0.70	0.53	0.52
193.5	31.7	CH_3COCN	0.63	0.50	0.46
193.0	32.1	CH_3COCN	0.60	0.47	0.39

- Good agreement between observed and calculated RRKM acetyl lifetimes:
 - ▶ based on experimentally derived E_{int}
 - ▶ better agreement with for rate $\langle k(E)\rho(E) \rangle$ than with $k(\langle E_{\text{int}} \rangle)$
- Unimolecular Dissociation of Acetyl from Acetyl Cyanide and Acetic Acetic
Consistent with RRKM Rate



Summary: Acetyl Cyanide and Acetic Acid

Short (<300 fs) parent excited state lifetimes observed for both

Acetyl Cyanide: assignment and excited state data are consistent

- Spectra + calcs: 194 nm transition: B* 7B rather than to 3s Rydberg state
- Isotropic products: transition moment direction relative to CN bond

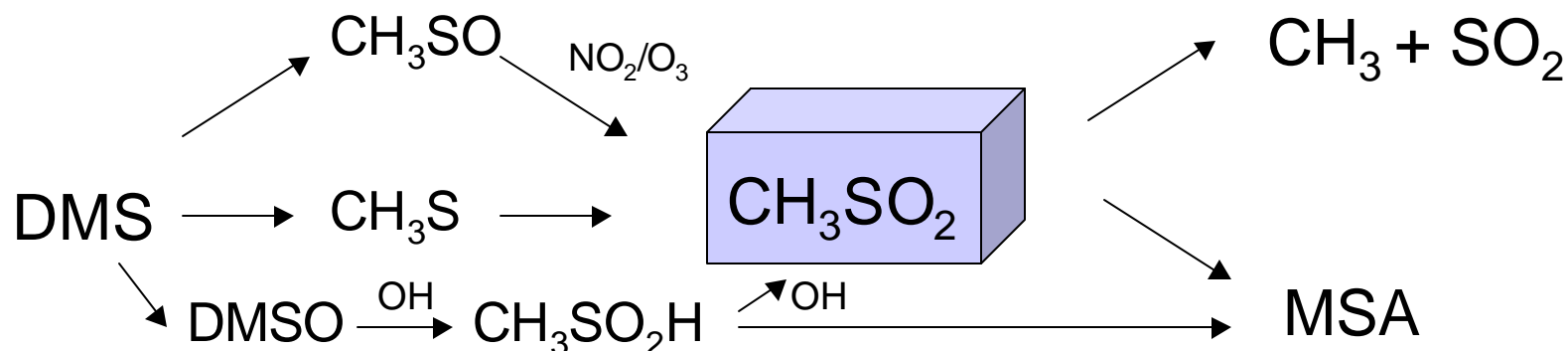
Acetyl from acetic acid and acetyl cyanide excited near 200 nm

- Measured and calculated RRKM rates dissociation rates agree
- Detailed comparison possible:
simple diatomics fragments - product energy measurements are available
- Dynamics appear nonstatistical for other precursors
acetone [*Kim et al.*] and acetyl chloride [*Suzuki and coworkers*]
- Implies state-specific, preparation-dependent behavior (extrinsic non-RRKM)
differences:
nature of excited state (Rydberg vs. valence)
fragment complexity, symmetry



Ultrafast Study of the Unimolecular Dissociation of Methyl Sulfonyl

- CH_3SO_2 : Possible intermediate in atmospheric sulfur chemistry and liquid photooxidation of DMS



- Spectroscopy and dynamics: few studies - not well characterized
 - ▶ liquid phase absorption
 - ▶ calculations of structures, energetics and vibrational freqs.
- Kinetics of CH_3SO_2 : *product* studies - not reactant

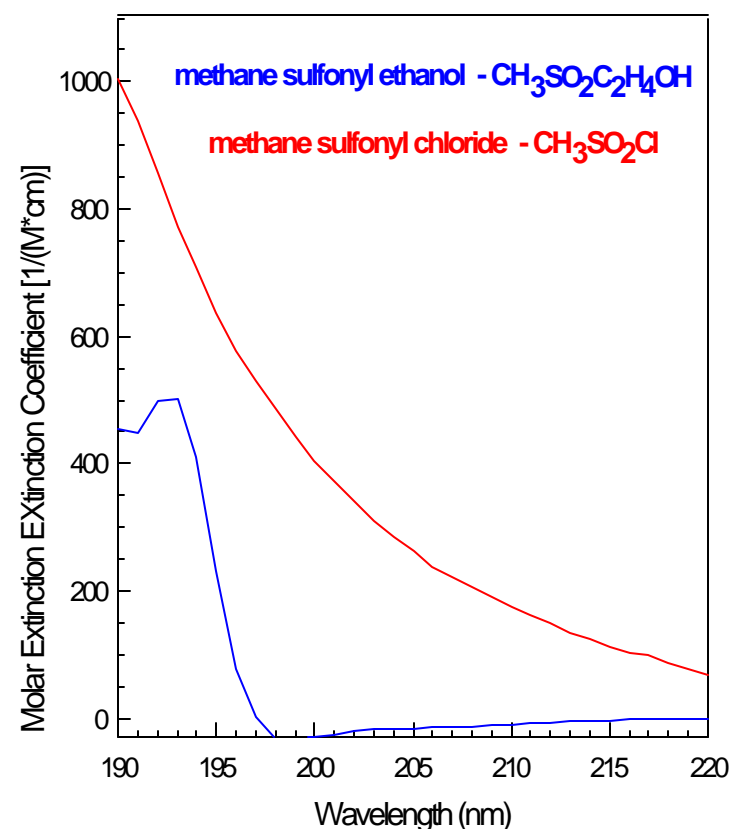


CH₃SO₂ Unimolecular Dynamics Study

- 1) Develop photolytic route to generate stable CH₃SO₂
- 2) Is CH₃SO₂ dissociation rate statistical/RRKM?

Deep UV fs photoionization study of dissociation dynamics

- Various precursors:
 - Methyl sulfonyl chloride (MSC)
 - Methyl sulfonyl ethanol (MSE)
- Measure dissociation rates: primary and secondary
- Fractional dissociation of MS (*i.e.*, stability) determined for each precursor

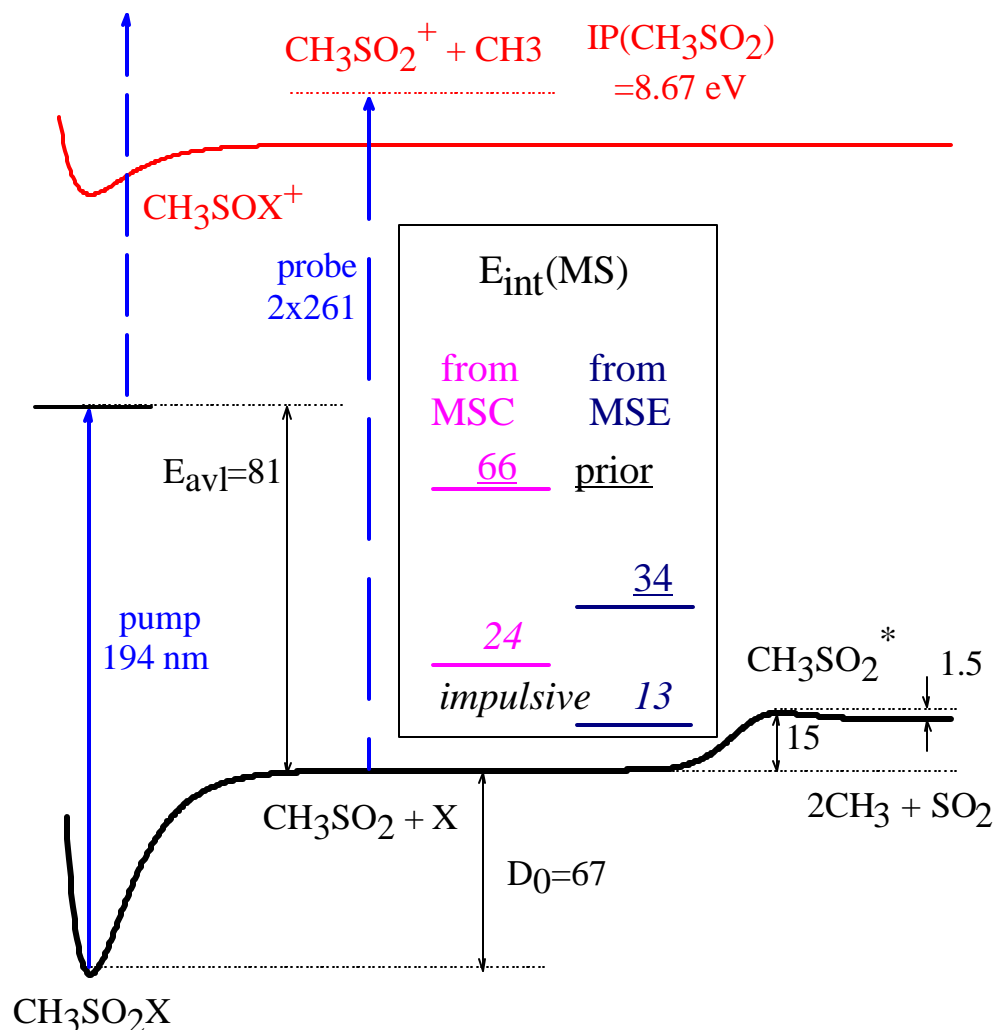




Methyl Sulfonyl Dissociation Dynamics

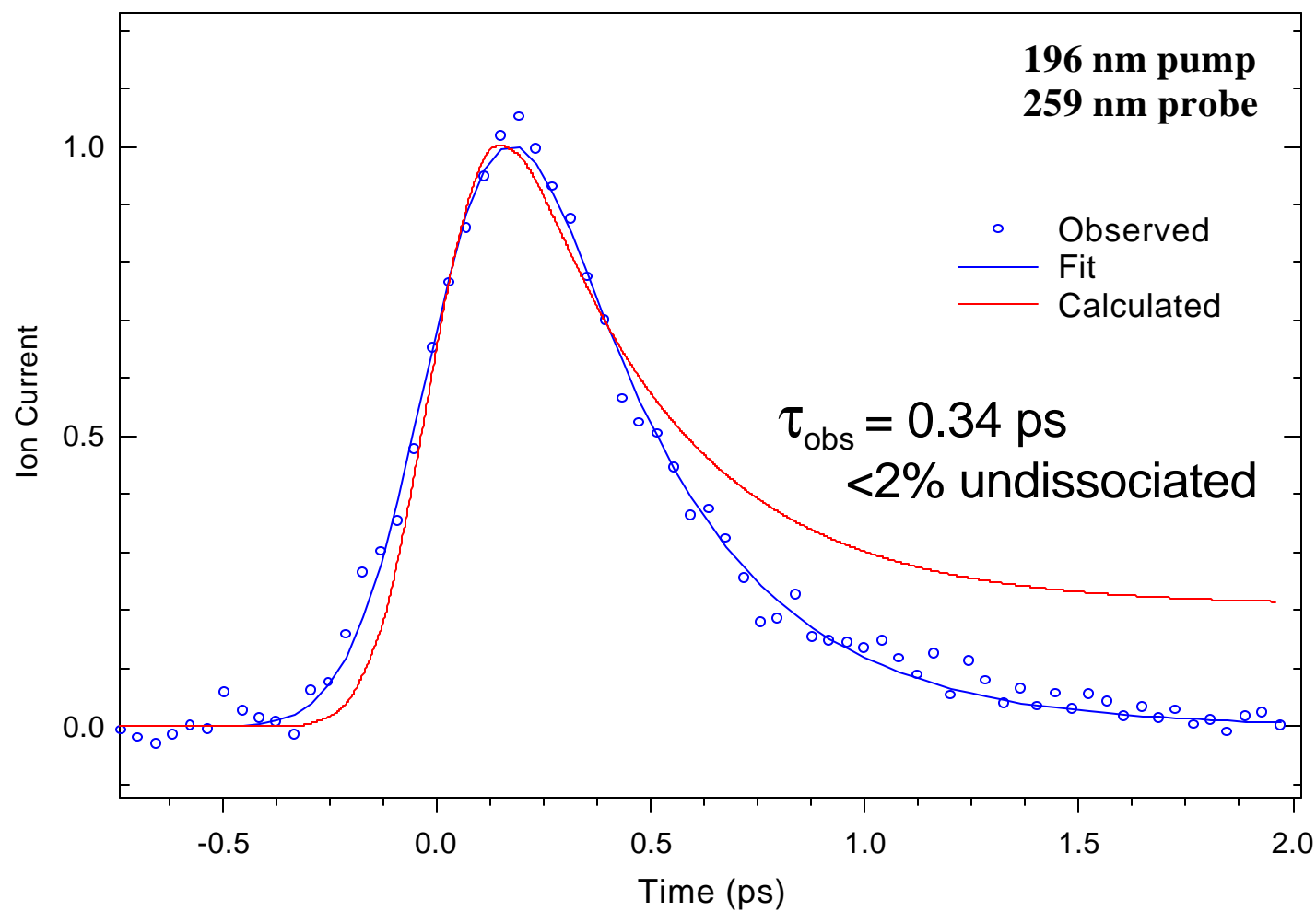
Compare measured and calc'd rates

- NO PRODUCT STUDIES:
 - Anything goes!
 - *Assume* energy partitioning
 - $\rho(E)$: impulsive and prior
- k_{uni} obs. vs. calc ($\langle k(E)\rho(E) \rangle$)
- fraction dissociation
- $k_{\text{calc}}(E)$: *ab initio* barrier and freqs
 - Davis
 - Marshall
 - Franck and Turcek



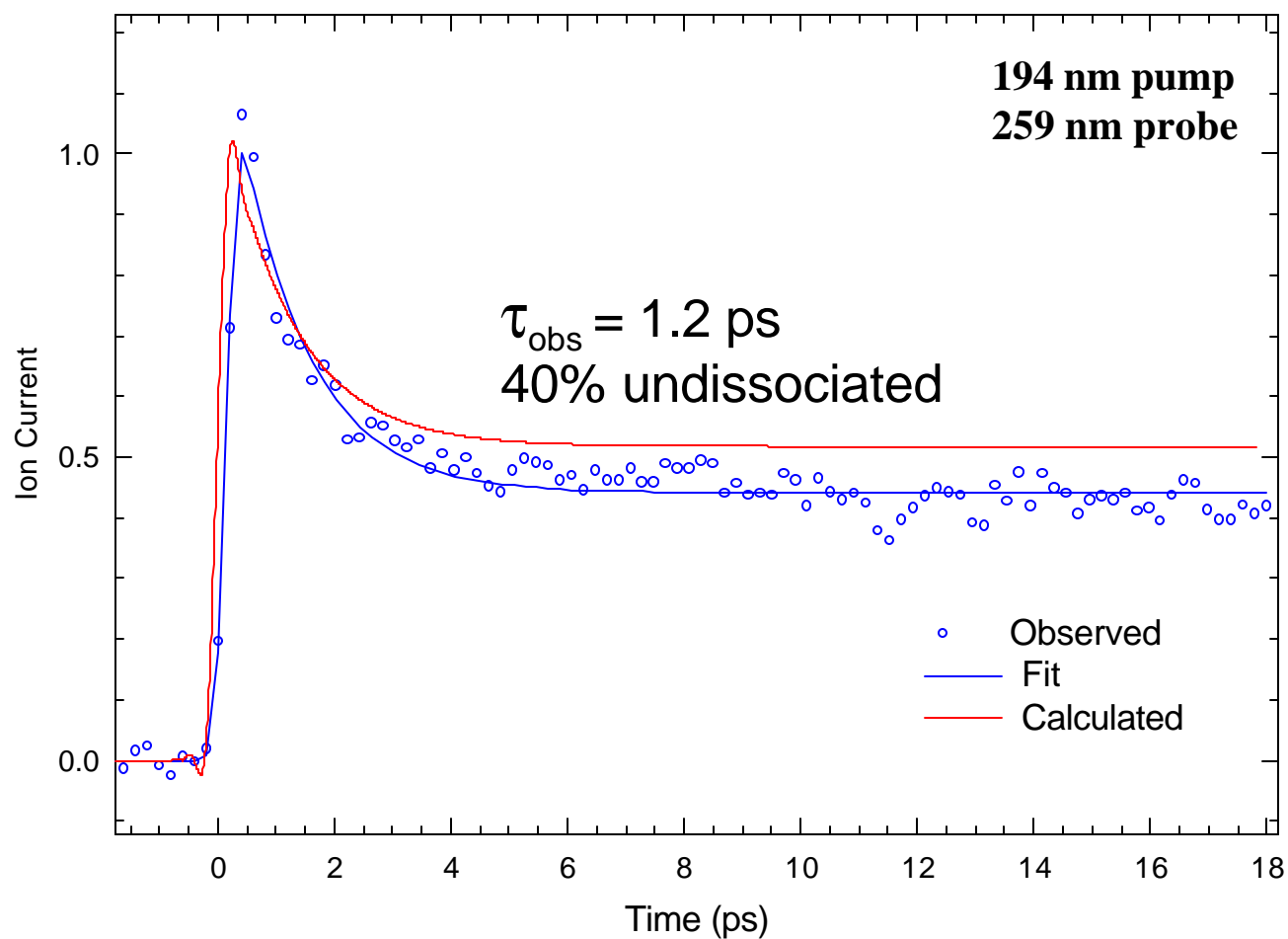


Ultrafast Photoionization: CH_3SO_2 from MS-Chloride





Ultrafast Photoionization: CH_3SO_2 from MS-EtOH





Summary for Methyl Sulfonyl Ultrafast Study

Dissociation rates and fractional dissociation MS:

Very close to calculations with impulsive/RRKM

Dissociation from prior - too much for MSE and too fast

Precursor	Calculated time (ps)	Observed time (ps)	Calc'd fraction undiss.	Obs. fraction undiss.
MSC	0.34	0.34	0.11	<0.02
MSE	1.2	1.2	0.46	0.40

- Dynamics: Calculations are **NOT** unique
fortuitous? unrestricted by expt. product energies
- MSE better than MSC for making methyl sulfonyl



Summary and Conclusions

Ultrafast Photoionization Studies of Unimolecular Dissociation

Directly measured dissociation rates:

- Correlate with results from product studies
 - ▶ primary dissociation: lifetimes and anisotropy
 - ▶ secondary/unimolecular dissociation:
 - most useful when internal energy known from product studies
 - direct comparison for same excitation conditions
- Acetyl dissociation - nonstatistical behavior is precursor dependent
 - ▶ preparation-specific: questions remain about how so
 - ▶ better candidate for control than otherwise
- Methyl sulfonyl can be generated from MSE
 - consistent with dynamics calculations